High-Speed Third-Order Nonlinear Optical Response Using Organic Solutions

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We have observed high-speed third-order nonlinear optical response using organic solutions of π-conjugated low-molecular-weight compounds. Optical Kerr shutter (OKS) measurement, third-harmonic generation (THG) measurement, and a degenerate four-wave mixing (DFWM) experiment were carried out to examine the high-speed response in several organic solutions. A comparison between the OKS and THG nonlinearities indicates that a long molecule increases the ratio of the fast electronic contribution in the all-Kerr nonlinearity. The fast response characteristics are confirmed by the DFWM experiment, thus showing that a long molecule successfully reduces the contribution of the molecular orientation effect with a slow relaxation time.

1. Introduction

Organic third-order nonlinear optical materials have shown a high potential for efficient optically gated optical switching.[1−5] In addition to their high efficiency, organic materials have also demonstrated excellent processability, high laser tolerance, and stability. However, the response mechanism of such materials, if we use them in a solution form, is often governed by the molecular contribution, such as the molecular orientation effect, and for this reason organic solutions tend to exhibit a relatively slow response time. In this Letter, by changing the molecular length of the π-conjugated low-molecular-weight compounds, we show that the slow molecular contribution of the organic solutions can be lessened for the observation of a high-speed third-order nonlinear optical response. We used carbon disulfide, nitrobenzene, and the saturated *N*,*N*-dimethylformamide (DMF) solutions of 4-(*N*,*N*-diethylamino)-β-nitrostyrene (DEANST) and terephthal-bis-(4-*N*,*N*-dihexylaminoaniline) (HH-SBA), whose molecular structures are shown in Figure 1. To investigate the response characteristics in these organic solutions, their third-order nonlinear coefficients were estimated by optical Kerr shutter (OKS) and third-harmonic generation (THG) measurements. Moreover, a degenerate four-wave mixing (DFWM) experiment was conducted to prove the high-speed response.

2. Experimental Section

The OKS measurement was done using a gate beam generated from a Nd:YAG laser (1.064-μm wavelength; 6-ns duration; 10-Hz repetition) and a Nd:YAG laser-pumped dye laser (0.70-μm wavelength; 6-ns duration; 10-Hz repetition). An AlGaAs laser diode pulse (0.81-μm wavelength; 50-ns duration), synchronized with the gate pulse, was used as a probe beam. The detector was a photomultiplier tube. The gate and probe power densities were around 50 MW/cm^2 and 100 W/cm^2, respectively. In calculating the OKS nonlinear refractive index n_{2B}(OKS), the probe transmittance intensity T was compared with the standard of carbon disulfide under the same gate power and medium length.[6,7] The Kerr nonlinearity n_{2B}(OKS) is obtained by

$$n_{2B}(\mathrm{OKS}) = \left(\frac{T}{T_s}\right)^{1/2} n_{2B,s}(\mathrm{OKS}) \tag{1}$$

Here, the subscript s means the standard of carbon disulfide.

The nonlinear refractive index n_2(THG), which is defined in terms of self-phase modulation (SPM),[7,8] was derived from the THG measurement. The difference-frequency generator consisting of a LiNbO$_3$ crystal provided a pump beam with a wavelength from 1.5 to 2.2 μm. We used the pump beam whose duration was 6 ns and repetition rate was 10 Hz. The third-harmonic (TH) wave was detected with a photomultiplier tube and a boxcar averager. The pump power density was varied from 50 to 100 MW/cm^2. The THG nonlinearity n_2(THG) was calculated by comparing the TH intensity with the standard of fused silica glass.[7−9] The n_2(THG) value is given by

$$n_2(\mathrm{THG}) = \left(\frac{n_s}{n}\right)^2 \left(\frac{n+1}{n_s+1}\right)^4 \frac{l_{c,s}}{l_c} \left(\frac{I_{3\omega}}{I_{3\omega,s}}\right)^{1/2} n_{2,s}(\mathrm{THG}) \tag{2}$$

where n is the linear refractive index, l_c is the coherence length, and $I_{3\omega}$ is the TH intensity. The subscript s indicates the standard medium.

The DFWM properties were examined at a wavelength of 0.81 μm. The beam was produced by the combination of a Ti:Al$_2$O$_3$ regenerative amplifier and an optical parametric amplifier. The pulse duration was 200 fs, and the repetition rate was 200 kHz. The pump power density ranged from 10 to 50 MW/cm^2. We detected the DFWM signal using the photomultiplier tube. The probe beam was delayed against the two pump beams for the estimation of the response time.

3. Results and Discussion

In the OKS measurement using solution media, the Kerr nonlinearity n_{2B}(OKS) is mainly given by the sum of the

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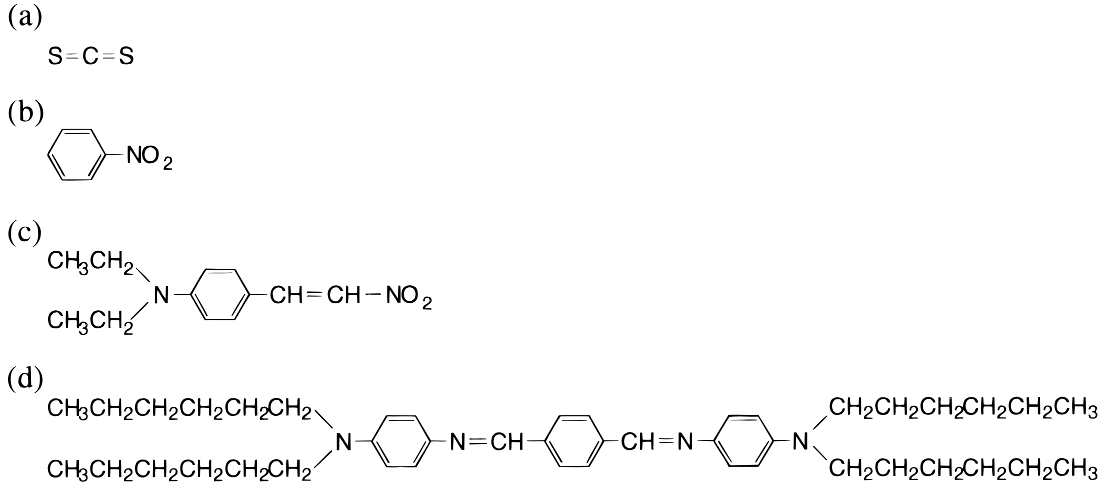

Figure 1. Molecular structures of (a) carbon disulfide, (b) nitrobenzene, (c) DEANST, and (d) HH-SBA. The molecular length changes by degrees. Each solution was poured into a 1-mm thick glass cell.

TABLE 1: Concentrations and the OKS and THG Nonlinearities[a]

solution	concn (mol/L)	n_{2B}(OKS) (cm^2/W)	n_2(THG) (cm^2/W)	$n_{2B}{}^{e}$(OKS)/ n_{2B}(OKS)
carbon disulfide	16	4.9×10^{-15}	6.7×10^{-16}	0.18
nitrobenzene	9.8	3.6×10^{-15}	5.4×10^{-16}	0.20
DEANST	2.8	5.2×10^{-14}	1.2×10^{-14}	0.31
HH-SBA	4.5×10^{-2}	5.7×10^{-13}	2.5×10^{-13}	0.58

[a] The nonlinearity was calculated for 1 M concentration. The long molecules of DEANST and HH-SBA provided increased 1 M nonlinearity itself in addition to a large $n_{2B}{}^{e}$(OKS)/n_{2B}(OKS) value.

electronic and molecular contributions

$$n_{2B}(\text{OKS}) = n_{2B}{}^{e}(\text{OKS}) + n_{2B}{}^{m}(\text{OKS}) \qquad (3)$$

where the first and second terms are the electronic and molecular contributions, respectively. Contrarily, in the THG measurement, since only the nonlinearity due to the electronic contribution can be detected, the THG nonlinearity n_2(THG) is represented by the electronic part of the SPM nonlinear refractive index $n_2{}^{e}$ as follows:[8]

$$n_2(\text{THG}) = n_2{}^{e} \qquad (4)$$

Therefore, using the relationship $n_{2B}{}^{e}(\text{OKS}) = (4/3)n_2{}^{e}$ (refs 7, 10), from eqs 3 and 4, we obtain the ratio of the electronic contribution in all-Kerr nonlinearity, $n_{2B}{}^{e}$(OKS)/n_{2B}(OKS), assuming that the wavelength dispersion of the nonlinearity can be ignored. The electronic contribution $n_{2B}{}^{e}$(OKS)/n_{2B}(OKS) is written as

$$\frac{n_{2B}{}^{e}(\text{OKS})}{n_{2B}(\text{OKS})} = \frac{4n_2(\text{THG})}{3n_{2B}(\text{OKS})} \qquad (5)$$

Table 1 shows the concentrations and the OKS and THG nonlinearities for carbon disulfide, nitrobenzene, and the DMF solutions of DEANST and HH-SBA. The $n_{2B}{}^{e}$(OKS)/n_{2B}(OKS) value was found to increase with increasing molecular length. In the case of carbon disulfide, the electronic contribution accounts for only $^1/_5$ of the Kerr nonlinearity, but in the solution of long HH-SBA molecule, the electronic contribution is almost $^3/_5$. Increasing molecular length will yield a larger $n_{2B}{}^{e}$(OKS)/n_{2B}(OKS) value.

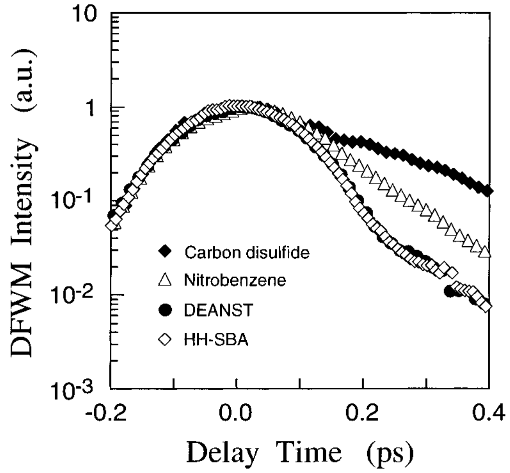

Figure 2. DFWM intensity as a function of the delay time for carbon disulfide, nitrobenzene, and the DMF solutions of DEANST and HH-SBA. The DFWM intensity decays fast in the solution consisting of long molecules. The DFWM signal of the DMF solvent is very weak compared with that of DEANST and HH-SBA molecules.

The molecular length dependence of the nonlinear property was further investigated by the DFWM experiment. Figure 2 shows the DFWM intensity as a function of the delay time. The magnitude of the DFWM intensity is normalized in this figure. The DFWM intensity was, for all the solutions, observed to change in proportion to the cubic of the pump intensity. We found a notable molecular length dependence; large molecules of DEANST and HH-SBA have a fast response time; that is, the component having a slow relaxation time is reduced for these large molecules. This molecular length dependence is explained as follows.

The optically induced refractive index change $\Delta n(t)$ in the DFWM experiment using solution media is phenomenologically described as[2]

$$\Delta n(t) = n_{2B}{}^{e}(\text{DFWM})\, I(t) + \sum_i (n_{2B,i}{}^{m}(\text{DFWM})/\tau_i) \int_{-\infty}^{t} I(t') \exp[-(t-t')/\tau_i]\, dt' \qquad (6)$$

Here, $n_{2B}{}^{e}$(DFWM) is the DFWM nonlinear refractive index. The first and second terms are the electronic and molecular contributions, respectively. The summation index i indicates the ith component of the molecular contribution. Although the

TABLE 2: Nonlinearity Ratios and Response Times τ for the Fast and Slow Components of the Molecular Contribution[a]

solution	fast-component ratio [τ_f(ps)]	slow-component ratio [τ_s(ps)]
carbon disulfide	0.20 [0.25]	0.62 [1.5]
nitrobenzene	0.20 [0.25]	0.60 [30]
DEANST	0.20 [0.60]	0.49 [100]
HH-SBA	0.30 [0.60]	0.12 [500]

[a] These results were obtained by fitting the DFWM data.

response time for the electronic contribution is less than subpicosecond, the molecular contribution, like the molecular orientation effect, has a relatively slow response time of more than the picosecond level. The response time τ_s for the molecular orientation effect is qualitatively represented by one-third the Debye relaxation time

$$\tau_s = \frac{\eta\nu}{k_B T} \tag{7}$$

where η is the viscosity of the solution, ν is the molecular volume, k_B is the Boltzmann constant, and T is the temperature of the solution. From eq 7, it is shown that, as the molecular length increases, the response time τ_s for the molecular orientation effect becomes slower. However, eq 6 points out that the contribution of the molecular orientation effect for the long molecules of DEANST and HH-SBA is negligible because of their large τ_s.

For our DFWM experimental setup, the DFWM signal is given by

$$I(t_d) \propto \int_{-\infty}^{\infty} I_p(t - t_d)\{\Delta n(t)\}^2 \, dt \tag{8}$$

where t_d is the delay time. Using eqs 6 and 8, the experimental data in Figure 2 can be fitted theoretically. The fitting results for the molecular contribution are summarized in Table 2. The ratio in the whole nonlinearity is shown for each nonlinear coefficient, and for the calculation, the electronic part was regarded to be equal to the $n_{2B}{}^e$(OKS)/n_{2B}(OKS) values listed in Table 1. We assumed that all the solutions have an electronic contribution as well as a molecular contribution consisting of two components, one fast and the other slow. The fast component of the molecular contribution is thought to be mainly due to the intermolecular interaction and intramolecular vibration.[11] The slow component originates from the molecular orientation effect. In Table 2, we can find that the long molecule has both the small nonlinearity ratio and the large τ_s value for the slow component of the molecular contribution (the molecular orientation effect). This finding leads to that, as understood from eq 6, the DEANST and HH-SBA solutions sufficiently decrease the influence of the molecular orientation effect, thereby exhibiting the fast response behavior. There is no noticeable difference between the DEANST and HH-SBA curves in Figure 2, which might suggest that the DEANST has a molecular length enough to yield a solution having a high-speed response time. Table 2 also shows that the response times for the molecular orientation effect for carbon disulfide and nitrobenzene agree with the typical reported values.[12-14] In addition, it is indicated that a long molecule has a large τ_f value for the fast component of the molecular contribution but that the τ_f value even for the long molecules of DEANST and HH-SBA is less than picosecond. Any slower decay than that originating from the molecular orientation effect was not seen in the DFWM experiment. Like in the OKS and THG measurements, the pump powers in the DFWM experiment using the DEANST and HH-SBA solutions were found to be several times smaller compared with that for carbon disulfide.

4. Conclusions

Third-order nonlinear optical properties of organic solutions using the π-conjugated low-molecular-weight compounds were investigated by means of OKS and THG measurements and a DFWM experiment. It was shown that the ratio of the fast electronic contribution in the all-Kerr nonlinearity is increased by using a long molecule. The largest 1 M n_{2B}(OKS) value of 5.7×10^{-13} cm^2/W was obtained with an HH-SBA solution. The DFWM experiment clarified that long molecules of DEANST and HH-SBA attain a high-speed response because the slow molecular orientation effect is effectively eliminated. It was also indicated that long molecules of DEANST and HH-SBA could feasibly provide an optical switching operation at low driving power.

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